

BH
20gibw

PATENT SPECIFICATION
NO DRAWINGS.

885,516



Date of Application and filing Complete Specification :
Jan. 16, 1958. No. 1511/58.

Complete Specification Published : Dec. 28, 1961.

Index at Acceptance:—Class 2(2), T2B.

International Classification:—C08b.

COMPLETE SPECIFICATION.

Higher Fatty Acid Esters of Dextran.

I, ARTHUR HENRY CLARKSON, a British Subject, of 14 Oxford Street, Nottingham, a Communicatee of The Commonwealth Engineering Company, a Corporation organized and existing under the laws of the State of Ohio, of 1771 Springfield Street, Dayton, Ohio, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to higher fatty acid esters of dextran having unexpectedly strong adherence to skin and to epidermal and albuminoidal proteins.

The esters of the invention contain an average of about 2.9 or 3.0 higher fatty acid radicals per anhydroglucose unit of the dextran.

The esters can be made by reacting dextran with a palmitic acid halide such as chloride. The reaction is carried out in the presence of an acid acceptor or binding agent. The acid acceptor may be an organic base, such as, for instance, a tertiary heterocyclic amine like quinoline, pyridine, or N-methyl morpholine. The reaction mass also comprises a substance in which the ester is at least partially solvated as it is formed. The presence of the partial solvent insures a substantially uniform, homogeneous reaction.

Substances which dissolve or swell the ester as it is formed are, for example, xylene, toluene, or dioxane.

The invention is based on the discovery that optimum esterification efficiency is obtained with equal parts of acid acceptor and swelling agent.

The reaction under the aforesaid conditions is carried out at 100° C. to 155° C.

for a period of time which varies inversely with the temperature used. Both the temperature employed and the reaction time depend on the boiling point of the mixture of acid acceptor and partial solvent used.

For instance, if such mixture consists of quinoline and xylene, the reaction is carried out by heating the mass at 150° C. to 155° C. for 30 minutes to an hour. When a mixture of pyridine and toluene is used the mass is preferably heated at 100° C. to 115° C. for one to three hours.

The dextran fatty acid ester at least partially dissolved in the crude reaction product can be isolated by washing the crude product with water to remove the organic base as the hydrochloride produced in the reaction, removing the aqueous layer, adding a solvent for the ester to the residue, and precipitating the resultant solution into a non-solvent for the ester.

A lower aliphatic alcohol, e.g., methanol, ethanol, isopropanol, may be used as precipitant. The precipitated ester is filtered off. It may be dried directly or further purified by re-precipitation and then dried.

These esters occur as white to light yellow granular solids. They are soluble in organic solvents, particularly of the non-polar type such as halogenated hydrocarbons, e.g. chloroform, carbon tetrachloride and mixed halides and such as those sold under the Registered Trade Mark "Freon" and in the common organic solvents such as benzene, toluene and the xylenes.

Although the dextran from which the fatty acid esters are derived may be water-soluble and is, in any case, hydrophilic, the esters are wholly hydrophobic. The esters show, also, an unexpectedly strong adherence to skin. When a solution of dextran palmitate containing an average of

BEST AVAILABLE COPY

about 2.9 palmitoyl radicals per anhydroglucose unit is applied to the skin in an organic solvent solution; evaporation of the solvent leaves a film of the ester deposited on the skin which cannot be removed by scrubbing with plain water, soapy water or abrasives like "Dutch Cleanser".

This resistance to water and aqueous media, which is very strong, and stronger than would be expected to result from the substitution of three of the fatty acid radicals on the units of a hydrophilic polysaccharide, may be due to the particular structure of dextran which, as is known, is made up of anhydroglucose units predominantly linked 1,6. That the structure of the present dextran is a contributing factor to the water-resistance and affinity for skin of the esters appears from the fact that the characteristics of films of the esters, i.e. the strong resistance to water, soap and abrasives, and the capacity to bond tenaciously to skin, are not strictly dependent on the molecular weight of the dextran. This is surprising, since it might have been expected that at least the resistance to water and aqueous media would depend on, or at least be influenced by, the total number of fatty acid radicals present in the end product. The overall number of such groups present increases with increase in the molecular weight of the dextran. Native, unhydrolyzed dextran produced microbiologically in the usual way by the action of dextran-synthesizing strains of *Leuconostoc* on sucrose has a molecular weight estimated in the millions. The number of anhydroglucose units of which it is comprised is extremely large, so that the total number of palmitoyl groups present in each molecule of the ester having an average palmitoyl radical content of 2.9 per unit of the dextran is also extremely large.

Dextran of lower molecular weight obtained, for example, by partial hydrolysis of the native dextran is comprised of a smaller number of anhydroglucose units. The overall fatty acid radical content per molecule of the dextran ester is correspondingly lower. Nevertheless, the resistance to water, soap, and abrasives of the esters derived from dextran hydrolyzates, such as those having an average molecular weight of 60,000 to 80,000 is substantially the same as is exhibited by the esters derived from native, unhydrolyzed dextran.

The strong adherence of these esters to skin and epidermal and albuminoidal surfaces, is not exhibited by similar esters of other parent substances. That property, as well as the resistance of the esters to water and aqueous media containing either soap or abrasives, apparently results from a combination of the specific structure of the dextran and the presence of about 3.0 of

the specific fatty acid radicals on substantially all of the units making up the dextran.

The presence of about 2.9 of the radicals of the palmitic acid on each of the anhydroglucose units of the dextran, appears to be critical. A native, unhydrolyzed dextran containing an average of only 2.0 palmitoyl or stearoyl radicals per anhydroglucose unit, does not have the adherence to skin that is exhibited by a palmitate of a hydrolyzed dextran of relatively low molecular weight, such as 60,000 to 80,000 and which contains about 3.0 palmitoyl radicals per anhydroglucose unit, even though, due to the extremely high molecular weight of the native dextran and the very large number of anhydroglucose units making up the molecule thereof, the overall content of palmitoyl radicals is higher. Evidently the presence of any substantial proportion of free hydroxyl groups not only decreases the hydrophobic property of the ester but also interferes with the capacity of the ester to adhere to the skin.

The present dextran esters resemble wax to the extent of having a slippery feel but unlike wax and wax-like materials generally are not emulsifiable with water using known emulsifying agents.

The resistance of the esters to water and aqueous media containing soap or abrasives adapts them to various important uses. The additional property of adhering tenaciously to skin both in the dry condition and when scrubbed with water, soap and water or even with abrasives, makes these esters particularly suitable for use in various cosmetic preparations, including lipsticks, rouge, liquid make-up preparations, creams, lotions, and so on. The esters are perfectly adapted to use as so-called chemical gloves, and have a special advantage for that use resulting from the natural affinity of the esters for skin, to which they impart a smooth, silky feel. Use of the esters in various textile applications, e.g., as soft finishing agents for fibers, fabrics and yarns, is also indicated.

The following example is given to illustrate specific embodiments of the invention.

Twenty gms. of hydrolyzed dextran having molecular weight between 20,000 and 200,000, average about 60,000 to 80,000, 100 gms. of palmitoyl chloride, 75 gms. of pyridine and 75 gms. of toluene are heated under reflux with vigorous agitation at 105° C.—110° C. for one and a half hours. The mixture is cooled rapidly to room temperature and washed with 250 mls. of water in a separatory funnel. The aqueous layer is removed. About 100 mls. of chloroform are added to the residue, with shaking to ensure that the residue is dissolved. The resulting solution is poured, with vigorous agitation, into a liter of methanol to pre-

5 cipitate the ester. The ester is collected on the Buchner funnel, redissolved in a mixture of 75 gms. of toluene and 100 mls. of chloroform, reprecipitated in methanol, collected and dried. On analysis, the dextran palmitate is found to contain an average of 2.9 palmitoyl radicals per anhydroglucose unit. It is very soluble in chloroform, carbon tetrachloride and "Freon", and soluble in benzene, toluene and the xylenes.

10 A film of the ester deposited on the hands from organic solvent is not removed by water, soap and water, or scouring with abrasives. It is entirely harmless to the skin and is an ideal chemical glove.

WHAT I CLAIM IS:—

1. A method of preparing an ester of dextran which comprises heating the dextran to 100° C. to 155° C. with a palmitic acid halide, in the presence of equal parts by weight of an acid acceptor and of a substance capable of dissolving or swelling the ester as it is formed, so as to produce a

dextran palmitate containing 2.9 palmitoyl radicals per anhydroglucose unit.

2. A method as defined by Claim 1 wherein the palmitic acid halide is palmitoyl chloride.

3. A method as defined by Claim 1 or Claim 2 wherein the acid acceptor is pyridine.

4. A method as defined by any of the preceding claims wherein the substance capable of dissolving or swelling the ester as it is formed is toluene.

5. A method of preparing an ester of dextran substantially as hereinbefore described in the example.

6. An ester of dextran prepared by the method of any preceding claim.

7. A composition adhesive to skin which comprises an ester according to Claim 6 dissolved in an organic solvent.

ERIC POTTER & CLARKSON,
Chartered Patent Agents.

Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1961.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies may be obtained.

This Page Blank (uspto)